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Abstract

The renormalization of electronic eigenenergies due to electron-phonon interactions (temperature dependence and zero-point motion effect) is important in many materials. We address it in the adiabatic harmonic approximation, based on first principles (e.g., density-functional theory), from different points of view: directly from atomic position fluctuations or, alternatively, from Janak's theorem generalized to the case where the Helmholtz free energy, including the vibrational entropy, is used.We prove their equivalence, based on the usual form of Janak's theorem and on the dynamical equation. We then also place the Allen-Heine-Cardona (AHC) theory of the renormalization in a first-principles context. The AHC theory relies on the rigid-ion approximation, and naturally leads to a self-energy (Fan) contribution and a Debye-Waller contribution. Such a splitting can also be done for the complete harmonic adiabatic expression, in which the rigid-ion approximation is not required. A n...

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Temperature dependence of electronic eigenenergies in the adiabatic harmonic approximation

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The renormalization of electronic eigenenergies due to electron-phonon interactions (temperature dependence and zero-point motion effect) is important in many materials. We address it in the adiabatic harmonic approximation, based on first principles (e.g., density-functional theory), from different points of view: directly from atomic position fluctuations or, alternatively, from Janak's theorem generalized to the case where the Helmholtz free energy, including the vibrational entropy, is used. We prove their equivalence, based on the usual form of Janak's theorem and on the dynamical equation. We then also place the Allen-Heine-Cardona (AHC) theory of the renormalization in a first-principles context. The AHC theory relies on the rigid-ion approximation, and naturally leads to a self-energy (Fan) contribution and a Debye-Waller contribution. Such a splitting can also be done for the complete harmonic adiabatic expression, in which the rigid-ion approximation is not required. A numerical study within the density-functional perturbation theory framework allows us to compare the AHC theory with frozen-phonon calculations, with or without the rigid-ion approximation. For the two different numerical approaches without non-rigid-ion terms, the agreement is better than 7 μeV in the case of diamond, which represent an agreement to five significant digits. The magnitude of the non-rigid-ion terms in this case is also presented, distinguishing specific phonon modes contributions to different electronic eigenenergies.

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I. INTRODUCTION

Electronic properties of solids and nanostructures can be computed from first principles with varying accuracies. In particular, the widespread GW approximation [1] within many-body perturbation theory describes electronic band gaps with errors in the range of 0.1–0.3 eV with respect to experiment [2]. Excitonic effects can be added based on the Bethe-Salpeter equation (BSE) [3]. However, a crucial ingredient is often disregarded: the electron-phonon interaction. Incidentally, the most advanced self-consistent GW calculations usually lead to overestimated band gaps [2], and most of the remaining discrepancy might be due to the electron-phonon interaction. Indeed, the influence of the lattice vibration at 0 K, known as the zero-point motion renormalization (ZPR), can be as large as 0.37 eV for the indirect band gap of diamond [4,5]. This correction often leads to a reduction of the band gap and hence might be crucial to correct the overestimations obtained with the self-consistent GW approximation.

The study of the direct effects of the electron-phonon interaction on the electronic structure has a long history. From the fifties to the late eighties, they were investigated and computed in a semiempirical context. It was first recognized that the temperature dependence of the electronic energies has two different origins: the volume expansion (studied by Shockley and Bardeen [6]) and the electron-phonon interactions at constant volume. In fact, the effect of the electron-phonon interaction at constant volume is usually the major contribution, and proves to be the most difficult to compute from first principles. This contribution is the focus of this paper.[1] In a pioneering work, Fröhlich introduced a model Hamiltonian that includes these interactions [7–9]. However, his approach leads to overscreening of phonon frequencies and involves empirical parameters [10].

In parallel, the self-energy contribution to electronic eigenenergy renormalization due to thermal vibrations was introduced by Fan [11,12]. His theory has no adjustable parameters and is based on the first-order perturbed Hamiltonian. Later, Cohen [13] used the Fan self-energy to compute the temperature dependence of the germanium band gap. Also, ideas from electron diffraction theories based on thermally averaged nuclear potentials lead Antončík [14] and others [15–17] to develop empirical Debye-Waller (DW) corrections to the nuclear potential. As these two lines of thought (Fan and DW) were developed independently of each other, only one of them was usually included in calculations.

At about the same time as Antončík, Brooks [18] emphasized that the electronic gap is actually a free energy difference with respect to varying occupation numbers of electronic and phononic levels. Furthermore, Allen and Hui [19] highlighted the equivalence between the action of the phonon population (atomic position fluctuations) on the electronic eigenenergies and the action of the electronic occupations on the phonon eigenfrequencies. This equivalence, that was later called Brook's theorem, was used in the eighties by several authors to discuss the temperature dependence of eigenenergies [19,20].

In 1974, Baumann [21] first suggested that both the Fan self-energy and DW terms were needed to describe the

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[1]Although first-principle studies of thermal expansion are not very frequent, the formalism is well established (at least for rather symmetric crystals, see, e.g, Rignanese *et al.* [78]).

influence of lattice vibrations on the electronic eigenenergies. Two years later, Allen and Heine [22] rigorously unified the theory and made the DW term translationally invariant. Their approach, combined with the rigid-ion approximation (RIA), which is valid for their semiempirical model, allows for a rewriting of the problem in terms of first-order derivatives of the effective potential only. Calculations of electron-phonon renormalization were then led by Cardona and coworkers [23–26], including Allen, based on physically motivated models [27,28] or on rigid-ion pseudopotentials approximations and empirical phonon models. The resulting approach is now called the Allen-Heine-Cardona (AHC) theory.

Until then, none of the calculation was based on first principles. In 1989, King-Smith *et al.* [20] computed the temperature-dependent band gap of Silicon using density-functional Theory (DFT) [29], by evaluating the change of phonon frequencies due to electronic occupations and invoking Brook's theorem.

It took more than one decade before other first-principle calculations were performed. Such studies relied on widely varying formalisms and methods, that can be broadly classified in three types, each with their distinct advantages and drawbacks. First, the temperature-dependent eigenenergies can be computed as a time average of the band gap obtained using first-principle molecular dynamics (MD) simulations. Using this method, Franceschetti [30] studied Si nanocrystals, Kamisaka *et al.* [31] studied CdSe and PbSe quantum dots, and Ibrahim [32] the temperature dependence of the optical response of GaAs. Ramírez *et al.* [33,34] simulated the temperature dependence of diamond and 3C-SiC band gap based on path-integral molecular dynamics (PIMD). This approach has the interesting characteristics that it includes effects beyond the harmonic approximation. Moreover, while normal molecular dynamics, which involves the harmonic approximation, wrongly delivers a classical Boltzmann statistics for phonons, the more computationally demanding PIMD properly includes nuclear quantum effects and delivers Bose-Einstein statistics for phonons. Thus, with PIMD, zero-point motion effects are observed. However, this MD (or PIMD) method is most suited for finite systems. Indeed, for solids, a supercell has to be used to sample the phonon wave-vector space, with a corresponding increase of the computational time and memory.

A second method uses frozen phonons (FP): the computation of the change of eigenenergies due to atomic displacements along the normal modes is followed by a Bose-Einstein weighted sum of the contribution of each mode. In 2005, Capaz *et al.* [35] studied the temperature dependence of carbon nanotube band gaps within the framework of a tight-binding method. Patrick *et al.* [36] examined diamondoids, and Han and Bester [37] studied various semiconductor nanoclusters, still using the FP method but this time with DFT simulations. Anharmonic electron-phonon contributions to the temperature dependence of the indirect band gap of diamond were also studied by Monserrat *et al.* [38] with the same methodology. Recently, Antonius *et al.* [39], still relying on the FP method, computed the renormalization of the diamond band gap within the GW approximation and observed a large increase of the renormalization with respect to DFT, in better agreement with experimental values. This result is in line with earlier estimations of many-body effects on the electron-phonon coupling in various systems [40–45].

As a third approach, the diagrammatic method of many-body perturbation theory, from which AHC originates, allowed Giustino *et al.* [46] to compute the ZPR and the temperature dependence of the diamond band gap with Wannier functions in the density-functional perturbation theory (DFPT) [47,48] framework. Marini *et al.* [49–52] focused on the dynamical effects, beyond the adiabatic approximation, which are absent from the two previous approaches (MD and FP).

There has been some confusion about the (non)-equivalence of these three approaches, in the first-principle context. Although the first (MD) and second (FP) one are equivalent when considered within the adiabatic harmonic approximation, the third one (AHC) is equivalent to the firsts *only* when the rigid-ion approximation is valid, which is not the case in the first-principle context. Indeed, Gonze *et al.* [53] pointed out that the FP and AHC formalisms differ by nondiagonal Debye-Waller terms, and computed these for simple diatomic molecules. In some cases, the nondiagonal Debye-Waller terms were as large as the sum of the other contributions. They also reformulated the AHC theory using Sternheimer equations instead of summations over empty states, which led to a significant speed-up of their calculations. The difference between AHC and FP was also examined in the above-mentioned study by Antonius *et al.* [39], where the global effect of the RIA on the ZPR was found to be rather small for the band gap of diamond. Recently, a thorough validation study by Poncé *et al.* [54], comparing different first-principle codes, allowed to resolve a persisting disagreement on the value of the ZPR for the direct band gap of diamond and established a value of -0.41 eV from AHC formalism on top of DFT [54]. The latter study also revealed the very slow convergence with respect to the number of $\mathbf{q}$ points (phonon wave vectors). This slow convergence is due to vanishing energy denominators that progressively appear as the sampling gets refined, especially close to extrema of the band structure. Such a slow convergence is not restricted only to the AHC method: many wave vectors should be taken into account for obtaining properly converged FP calculations as well, while huge supercells should be used in the case of MD-based approaches.

Finally, the phonon-induced lifetime broadening of the electronic states derived from the imaginary part of the Fan self-energy was investigated by Lautenschlager [55,56] in a semi-empirical context, and, more recently, by Giustino [57] and Restrepo [58,59] with a first-principles implementation.

In this paper, we will clarify and establish links between the different first-principles approaches, for semiconductors and insulators. Strictly speaking, because of the adiabatic approximation, our theory does not apply to metals, as the phonon frequencies cannot be neglected with respect to electronic excitations. The same limitation is also encountered for semiconductors and insulators with a temperature sufficiently high to create a non-negligible population of holes and conduction electrons. So, provided the adiabatic approximation is valid, we establish Brook's theorem, and provide a detailed analysis of the difference between the AHC approach and the FP approach, elaborating on the brief results presented in Ref. [53]. Detailed DFT numerical results for

diamond will also be provided, going, for DFT, further than Ref. [39].

The structure of the paper is as follows. Section II examines Brooks theorem, which relies, at the first-principles level, on Janak's theorem generalized to the case where the free energy including the vibrational entropy is used, instead of a purely electronic expression. Section III links the equations of Sec. II with the AHC theory, in the periodic case (with notations suitable for later practical implementations) and also explores rigorously the rigid-ion approximation. In particular, one distinguishes the Fan contribution, the rigid-ion Debye-Waller contribution, and the non-rigid-ion Debye-Waller contribution. The sum over a large number of bands, present in the AHC theory, can be reduced drastically, by complementing it with an expression based on the projection over high energy bands of the first-order wave functions, in the spirit of the Sternheimer equation. Section IV establishes the connection between those equations and an equivalent finite-difference approach. Then, this connection is used in Sec. V to validate the theory of Sec. III as well as its implementation by comparison with finite-difference calculations for the case of diamond. This section also allows one to assess the importance of the rigid-ion approximation in the case of periodic solids. All equations derived in this work are expressed in Hartree atomic units where $m_e = \hbar = e = 1$.

II. TEMPERATURE-DEPENDENT ELECTRONIC EIGENENERGIES IN THE ADIABATIC HARMONIC APPROXIMATION

Brook's theorem states that the shift in an electronic eigenenergy (labeled n) due to the electron-phonon interaction, when a phonon is added in a phononic mode (labeled m), is equivalent to the shift in the m phonon mode eigenfrequency when an electron is placed in the n level, also caused by the electron-phonon interaction. Namely [18–20],

$$\frac{\partial \varepsilon_n}{\partial n_m} = \frac{\partial \omega_m}{\partial f_n}, \tag{1}$$

ε_n and f_n being respectively the eigenenergy and the thermal average of the occupation of the electronic state n, while ω_m and n_m are the eigenfrequency and the thermal average of the phononic occupation of the phonon mode m, respectively.

In this section, we detail this equality in a first-principles context: the phonons are obtained in the harmonic adiabatic approximation from the interatomic force constants, which are themselves second-order derivatives of the Born-Oppenheimer total energy, from which the electronic occupation effects can be traced explicitly.

We decided, for pedagogical reasons, to work in this section with isolated systems but the extension to periodic systems is straightforward using the convention of the appendices A 2 and A 3.

A. Fluctuations of atomic positions

The eigenfrequencies ω_m and unitless mass-scaled eigendisplacements $\xi_{m,\kappa\alpha}$ for the phonon mode m can be obtained from the dynamical equation [60]

$$\sum_{\kappa\alpha} D^{\kappa\alpha}_{\kappa'\gamma}\, \xi_{m,\kappa\alpha} = \omega_m^2 \xi_{m,\kappa'\gamma}, \tag{2}$$

where κ and κ' label atoms in the unit cell, α and γ label the cartesian spatial dimensions, and $D^{\kappa\alpha}_{\kappa'\gamma}$ are the mass-scaled interatomic force constants.

The mass-scaled quantities are expressed as follows:

$$\begin{aligned} \xi_{m,\kappa\alpha} &= \sqrt{M_\kappa} U_{m,\kappa\alpha}, \\ D^{\kappa\alpha}_{\kappa'\gamma} &= \frac{1}{\sqrt{M_\kappa}} C^{\kappa\alpha}_{\kappa'\gamma} \frac{1}{\sqrt{M_{\kappa'}}}, \end{aligned} \tag{3}$$

where M_κ is the mass of atom κ, $U_{m,\kappa\alpha}$ is the phonon eigendisplacements, and

$$C^{\kappa\alpha}_{\kappa'\gamma} = \frac{\partial^2 E^{\mathrm{BO}}}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}}, \tag{4}$$

are the interatomic force constants (IFC), where E^{BO} is the Born-Oppenheimer energy of the system (which excludes the kinetic energy of the nuclei), computed from first principles and $R_{\kappa\alpha}$ is the coordinate α of the atom κ. Using the fact that the mass-scaled eigendisplacements $\xi_{m,\kappa\alpha}$ are orthonormal and complete, the phonon frequencies can be obtained from

$$\omega_m^2 = \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} U^*_{m,\kappa'\gamma} C^{\kappa\alpha}_{\kappa'\gamma} U_{m,\kappa\alpha} \tag{5}$$

and the normalization of phonon eigendisplacements is

$$\sum_{\kappa\alpha} M_\kappa U^*_{m,\kappa\alpha} U_{m',\kappa\alpha} = \delta_{mm'}. \tag{6}$$

Within the harmonic approximation, where normal modes are decoupled from each other, we express the static temperature dependence of the eigenenergies $\varepsilon_n(T)$ as a thermal average of the value of the position-dependent eigenenergies $\tilde{\varepsilon}_n[z\mathbf{U}]$, where $z\mathbf{U}$ denotes generically a displacement from the equilibrium atomic positions:

$$\varepsilon_n(T) \triangleq \langle \tilde{\varepsilon}_n[z\mathbf{U}] \rangle (T) \tag{7}$$

$$= \sum_m^{3N} \frac{1}{\mathcal{Z}_m} \sum_{s_m} e^{\frac{-(s_m+1/2)\omega_m}{k_B T}} \times \int \chi^*_{m,s_m}(z) \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}] \chi_{m,s_m}(z) dz, \tag{8}$$

where N is the number of atoms, T is the temperature, s_m is the integer occupation of phonon mode m, $\mathcal{Z}_m = \sum_{s_m} e^{\frac{-(s_m+1/2)\omega_m}{k_B T}}$ is the mode-partition function, k_B is the Boltzmann's constant, $\chi_{m,s_m}(z)$ is the phonon eigenfunctions, z is the spatial coordinate associated with a phonon mode, and where bold symbols like $\mathbf{U}_{m,\kappa}$ denote Cartesian vectors.

We can expand the eigenenergies $\tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]$ of Eq. (7) in a Taylor series up to second order in z, since we are working within the harmonic approximation

$$\tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}] = \tilde{\varepsilon}_n[0] + z \frac{d}{dz} \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0} + \frac{1}{2} z^2 \frac{d^2}{dz^2} \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0}, \tag{9}$$

and insert it in Eq. (7). Using the properties of phononic wave functions in a harmonic potential (see Appendix A 1 for more details), we obtain

$$\varepsilon_n(T) = \tilde{\varepsilon}_n[0] + \frac{1}{2}\sum_m^{3N} \frac{1}{\mathcal{Z}_m \omega_m} \frac{d^2}{dz^2}\tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0} \times \sum_{s_m} e^{-(s_m+1/2)\alpha_m}\left(\frac{2s_m+1}{2}\right), \quad (10)$$

where we have defined $\alpha_m \triangleq \frac{\omega_m}{k_B T}$.

For sake of brevity, we introduce the notation $\Delta\varepsilon_n(T) \triangleq \varepsilon_n(T) - \tilde{\varepsilon}_n[0]$. Using the properties of geometrical series to evaluate the sum over s_m, $\Delta\varepsilon_n(T)$ becomes

$$\Delta\varepsilon_n(T) = \frac{1}{2}\sum_m^{3N} \frac{1}{\frac{e^{-\alpha_m/2}}{1-e^{-\alpha_m}}\omega_m} \frac{d^2}{dz^2}\tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0} e^{-\alpha_m/2} \times \left(\frac{e^{-\alpha_m}}{(1-e^{-\alpha_m})^2} + \frac{1}{2(1-e^{-\alpha_m})}\right), \quad (11)$$

which simplifies to

$$\Delta\varepsilon_n(T) = \sum_m^{3N} \frac{1}{2\omega_m} \frac{d^2}{dz^2}\tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0}\left(n_m(T)+\frac{1}{2}\right), \quad (12)$$

where we have introduced the Bose-Einstein distribution

$$n_m(T) = \frac{1}{e^{\frac{\omega_m}{k_B T}} - 1}. \quad (13)$$

We can consider the phonon occupation numbers $n_m(T)$ as independent variables in this expression, in which case,

$$\frac{\partial\varepsilon_n}{\partial n_m} \triangleq \frac{\partial\varepsilon_n(T)}{\partial n_m(T)} = \frac{1}{2\omega_m}\frac{d^2}{dz^2}\tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0}, \quad (14)$$

where we have defined the short-hand notation on the left-hand side of the equation because, even though each term in the derivative depends on the temperature, the derivative itself does not. Equation (12) can thus be written as

$$\Delta\varepsilon_n(T) = \sum_m^{3N} \frac{\partial\varepsilon_n}{\partial n_m}\left(n_m(T)+\frac{1}{2}\right). \quad (15)$$

Then, the zero-point motion contribution is simply the shift of the eigenenergies at $T = 0$, that is,

$$\Delta\varepsilon_n(T=0) = \frac{1}{2}\sum_m^{3N} \frac{\partial\varepsilon_n}{\partial n_m}, \quad (16)$$

highlighting that $\varepsilon_n(T=0) \neq \varepsilon_n[0]$. Additionally, from Eqs. (5) and (6), we can see that $\omega \propto M^{-1/2}$. Also, $\mathbf{U} \propto M^{-1/2}$ and the $z\mathbf{U}$ must have the dimension of length because it is an ionic displacement [see Eq. (12)]. Therefore z must have the dimension of $M^{1/2}$ times length. All of this leads to the fact that the ZPR of Eq. (12) goes as $(\omega M)^{-1} \propto M^{-1/2}$. This "isotopic effect" allows for experimental measurements of the zero-point renormalization by substituting atoms with heavier isotopes, as explained in the review paper of Cardona and Thewalt [5].

B. Eigenenergies as derivatives with respect to electronic occupation numbers f_n

Following Janak, we extend to fractional occupations the first-principle Born-Oppenheimer energy E^{BO}. Janak's theorem [61] then gives

$$\varepsilon_n = \frac{\partial E^{\mathrm{BO}}}{\partial f_n}, \quad (17)$$

where it has to be noted that the Janak theorem breaks down, within DFT, if the exact exchange-correlation functional (or any nonanalytic functional with respect to the occupation) is used. In that case, the total energy is not a continuous function of the electronic occupation anymore and eigenenergies must be defined as differences of total energies with integral occupations numbers.

We now complement the Born-Oppenheimer energy with phonon energy and entropy at the harmonic level. The energy becomes

$$E(T) = E^{\mathrm{BO}} + E_{\mathrm{vib}}(T) = E^{\mathrm{BO}} + \sum_m^{3N}\omega_m\left(n_m(T)+\frac{1}{2}\right), \quad (18)$$

where E^{BO} is the total energy without phonon and electron-phonon contributions. Taking into account the vibrational entropy gives a Helmholtz free energy [62]

$$F(T) \triangleq E(T) - T S_{\mathrm{vib}}(T), \quad (19)$$

where S_{vib} is the vibrational entropy,

$$S_{\mathrm{vib}}(T) = k_B \sum_m^{3N} ((1+n_m(T))\ln(1+n_m(T)) - n_m(T)\ln(n_m(T))). \quad (20)$$

We now show that the temperature-dependent eigenenergies can be obtained from the extension of Janak's theorem to finite phonon temperatures:

$$\varepsilon_n(T) = \frac{\partial F(T)}{\partial f_n}. \quad (21)$$

For sake of simplicity, we neglect the dependence of the Born-Oppenheimer energy E^{BO} on electronic temperature. Actually, the explicit treatment of the electron system at finite temperatures (e.g., using the Mermin functional [63]), supposing (wrongly) the adiabatic approximation to be still valid, would not change the remaining of the paper. Using this definition of $\varepsilon_n(T)$, Eq. (18), Eq. (19), and taking into account the dependence of the phonon frequencies on electronic occupation numbers as well as the dependence of phonon occupation numbers on electronic occupation numbers, the change of eigenenergies due to electron-phonon interaction becomes

$$\Delta\varepsilon_n(T) = \sum_m^{3N}\left(\frac{\partial\omega_m}{\partial f_n}\left(n_m(T)+\frac{1}{2}\right) + \omega_m\frac{\partial n_m(T)}{\partial f_n} - T\frac{\partial S_{\mathrm{vib}}}{\partial n_m(T)}\frac{\partial n_m(T)}{\partial f_n}\right). \quad (22)$$

Substituting Eq. (20) for $S_{\rm vib}$ into Eq. (22) gives

$$\Delta\varepsilon_n(T) = \sum_m^{3N} \left(\frac{\partial\omega_m}{\partial f_n} \left(n_m(T) + \frac{1}{2} \right) + \omega_m \frac{\partial n_m(T)}{\partial f_n} - k_B T \frac{\partial n_m(T)}{\partial f_n} \ln\left(\frac{1+n_m(T)}{n_m(T)} \right) \right). \quad (23)$$

Using Eq. (13), the last two terms in the sum cancel out. We thus obtain

$$\Delta\varepsilon_n(T) = \sum_m^{3N} \frac{\partial\omega_m}{\partial f_n} \left(n_m(T) + \frac{1}{2} \right). \quad (24)$$

This is the first important result of the present paper. To the authors knowledge, it was never derived starting from the free energy Eq. (19) and the finite temperature extension of Janak's theorem Eq. (21). Identification of Eq. (24) with Eq. (15) obviously yields

$$\frac{\partial\varepsilon_n}{\partial n_m} = \frac{\partial\omega_m}{\partial f_n}. \quad (25)$$

This link can be more rigorously established as follows. The derivative of the phonon frequency is retrieved from deriving Eq. (5) with respect to the electronic occupation:

$$2\omega_m \frac{\partial\omega_m}{\partial f_n} = \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \frac{\partial C^{\kappa\alpha}_{\kappa'\gamma}}{\partial f_n} U^*_{m,\kappa'\gamma} U_{m,\kappa\alpha}, \quad (26)$$

where the derivative of the displacements $U_{m,\kappa\alpha}$ with respect to the occupations f_n does not contribute thanks to the Hellmann-Feynman theorem [64,65]. The temperature dependence of the eigenenergies is obtained by substituting the preceding result for $\frac{\partial\omega_m}{\partial f_n}$ into Eq. (24):

$$\Delta\varepsilon_n(T) = \sum_m^{3N} \frac{1}{2\omega_m} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} U^*_{m,\kappa'\gamma} \frac{\partial C^{\kappa\alpha}_{\kappa'\gamma}}{\partial f_n} U_{m,\kappa\alpha} \left(n_m(T) + \frac{1}{2} \right). \quad (27)$$

Using Janak's theorem, we can reformulate the derivative of the IFC into derivatives of eigenenergies:

$$\frac{\partial C^{\kappa\alpha}_{\kappa'\gamma}}{\partial f_n} = \frac{\partial}{\partial f_n} \left(\frac{\partial^2 E^{\rm BO}}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}} \right) = \frac{\partial^2\varepsilon_n}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}}. \quad (28)$$

Substituting the above expression into Eq. (27), we obtain

$$\Delta\varepsilon_n(T) = \sum_m^{3N} \frac{1}{2\omega_m} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} U^*_{m,\kappa'\gamma} \frac{\partial^2\varepsilon_n}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}} \times U_{m,\kappa\alpha} \left(n_m(T) + \frac{1}{2} \right). \quad (29)$$

The double sum over atomic position displacements is actually the second-order derivative of the eigenenergy with respect to the normal mode,

$$\sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} U^*_{m,\kappa'\gamma} \frac{\partial^2\varepsilon_n}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}} U_{m,\kappa\alpha} = \frac{d^2}{dz^2} \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0}, \quad (30)$$

so that we recover, from Eqs. (14), (25), and (30) the following relations:

$$\frac{\partial\varepsilon_n}{\partial n_m} = \frac{1}{2\omega_m} \frac{d^2}{dz^2} \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\big|_{z=0} = \frac{1}{2\omega_m} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} U^*_{m,\kappa'\gamma} \frac{\partial^2\varepsilon_n}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}} U_{m,\kappa\alpha} = \frac{\partial\omega_m}{\partial f_n}. \quad (31)$$

We thus obtain a demonstration of Brook's theorem in the first-principles context.

C. The Fan and Debye-Waller contributions

In order to establish links with the Fan, Debye-Waller, and AHC approaches, we now analyze Eq. (29) in more detail, focusing on the second-order derivative of the eigenenergies with respect to two atomic displacements. The latter can be obtained from perturbation theory, starting from

$$\varepsilon_n = \langle \Psi_n | \hat{H} | \Psi_n \rangle. \quad (32)$$

The first step is to differentiate and use the Hellmann-Feynman theorem. This yields, at equilibrium geometry,

$$\frac{\partial\varepsilon_n}{\partial R_{\kappa\alpha}} = \left\langle \Psi^{(0)}_n \middle| \frac{\partial\hat{H}}{R_{\kappa\alpha}} \middle| \Psi^{(0)}_n \right\rangle. \quad (33)$$

Equation (33) can be derived a second time, with respect to another atomic displacement. An equivalent result can be obtained by switching the two atomic displacements. Both can be combined and deliver an expression that is real and explicitly symmetric with respect to the indices $\kappa\alpha$ and $\kappa'\gamma$:

$$\frac{\partial^2\varepsilon_n}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}} = \left\langle \Psi^{(0)}_n \middle| \frac{\partial^2\hat{H}}{\partial R_{\kappa\alpha} R_{\kappa'\gamma}} \middle| \Psi^{(0)}_n \right\rangle + \frac{1}{2} \left(\left(\left\langle \frac{\partial\Psi_n}{\partial R_{\kappa\alpha}} \middle| \frac{\partial\hat{H}}{\partial R_{\kappa'\gamma}} \middle| \Psi^{(0)}_n \right\rangle + (\kappa\alpha) \leftrightarrow (\kappa'\gamma) \right) + \text{c.c.} \right), \quad (34)$$

where $(\kappa\alpha) \leftrightarrow (\kappa'\gamma)$ stands for the previous term in which the indices $\kappa\alpha$ and $\kappa'\gamma$ have been exchanged, and where c.c. stands for the complex conjugate of the previous term.

The contribution from the second-order perturbation of the Hamiltonian, $\frac{\partial^2\hat{H}}{\partial R_{\kappa\alpha} R_{\kappa'\gamma}}$, gives the Debye-Waller (DW) term [14,66] of the semiempirical approach. The other bracketed term originates from the first-order modifications of the wave function and corresponds to the Fan term when considered in many-body perturbation theory. As mentioned in the introduction, the complementarity of the two terms for the description of the eigenenergy renormalization due to the electron-phonon interaction, although obvious in the present derivation, was first shown in 1974 by Baumann [21].

III. FROM THE ADIABATIC APPROXIMATION TO THE ALLEN-HEINE-CARDONA THEORY

In this section, we relate Eq. (29) to the AHC theory, as formulated[2] by Giustino *et al.* [46]. We also carefully treat

[2] Although we agree with Eqs. (2)–(7) of Allen and Cardona [23], we think that their Eq. (8) is erroneous, since the polarization vectors in

the RIA and unveil the terms it neglects. Furthermore, we discuss the translational invariance and its consequences. In order to focus on solids (in view of the application and testing for diamond and solid-state systems in general), we work with periodic systems and introduce the related definitions. More information in this respect is provided in Appendixes A 2 and A 3.

A. Wave vectors and translational invariance

We introduce a specific notation for the derivative of an arbitrary quantity X that depends on the atomic coordinates, with respect to a collective displacement of atoms characterized by a wave vector $\mathbf{q}$,

$$\frac{\partial X}{\partial R_{\kappa\alpha}(\mathbf{q})} = \frac{1}{N_{\mathrm{BvK}}} \sum_{l} e^{i\mathbf{q}\cdot\mathbf{R}_l} \frac{\partial X}{\partial R_{l\kappa\alpha}}, \tag{35}$$

where $R_{l\kappa\alpha}$ is the coordinate along the α axis of the atom κ in the cell l, and N_{BvK} is the number of primitive cells of the periodic system defined by the Born-von Karman boundary conditions [67].

The eigendisplacement vectors are solution of the dynamical equation

$$\sum_{\kappa\alpha} \tilde{C}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) = M_{\kappa'} \omega^2_{m\mathbf{q}} U_{m,\kappa'\gamma}(\mathbf{q}), \tag{36}$$

where the Fourier transform of the IFC appears

$$\begin{aligned} \tilde{C}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) &= \frac{1}{N_{\mathrm{BvK}}} \sum_{ll'} C_{\substack{l\kappa\alpha \\ l'\kappa'\gamma}} e^{-i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} \\ &= \sum_{l'} C_{\substack{0\kappa\alpha \\ l'\kappa'\gamma}} e^{i\mathbf{q}\cdot\mathbf{R}_{l'}} \\ &= N_{\mathrm{BvK}} \frac{\partial^2 E^{\mathrm{BO}}}{\partial R_{\kappa'\alpha}(-\mathbf{q}) \partial R_{\kappa''\beta}(\mathbf{q})}, \end{aligned} \tag{37}$$

where $\mathbf{R}_l$ is a translation vector of the Bravais lattice. The eigendisplacement vectors fulfill the following normalization condition:

$$\sum_{\kappa\alpha} M_\kappa U^*_{m,\kappa\alpha}(\mathbf{q}) U_{m',\kappa\alpha}(\mathbf{q}) = \delta_{mm'}. \tag{38}$$

All properties of a crystal, including its eigenenergies and their derivatives, must be invariant upon a uniform translation $\boldsymbol{\delta}$. Therefore

$$\varepsilon_{n\mathbf{k}}[\{\mathbf{R}_{l\kappa}\}] = \varepsilon_{n\mathbf{k}}[\{\mathbf{R}_{l\kappa} + \boldsymbol{\delta}\}], \tag{39}$$

$$\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial R_{\kappa'\alpha}(\boldsymbol{\Gamma})}[\{\mathbf{R}_{l\kappa}\}] = \frac{\partial \varepsilon_{n\mathbf{k}}}{\partial R_{\kappa'\alpha}(\boldsymbol{\Gamma})}[\{\mathbf{R}_{l\kappa} + \boldsymbol{\delta}\}]. \tag{40}$$

In Eq. (40), we have taken the derivative with respect to a collective displacement of atoms that does not break the translation symmetry ($\mathbf{q} = \boldsymbol{\Gamma}$) to avoid any problem with the Bloch theorem, and keep the Bloch notation $n\mathbf{k}$.

By Taylor expanding the right-hand side of Eq. (40), we obtain

$$\begin{aligned} \frac{\partial \varepsilon_{n\mathbf{k}}}{\partial R_{\kappa'\alpha}(\boldsymbol{\Gamma})}[\{\mathbf{R}_{l\kappa} + \boldsymbol{\delta}\}] &= \frac{\partial \varepsilon_{n\mathbf{k}}}{\partial R_{\kappa'\alpha}(\boldsymbol{\Gamma})}[\{\mathbf{R}_{l\kappa}\}] \\ &+ \sum_{\kappa''\beta} \delta_\beta \frac{\partial^2 \varepsilon_{n\mathbf{k}}}{\partial R_{\kappa'\alpha}(\boldsymbol{\Gamma}) \partial R_{\kappa''\beta}(\boldsymbol{\Gamma})}[\{\mathbf{R}_{l\kappa}\}] + \mathcal{O}(\boldsymbol{\delta}^2), \end{aligned} \tag{41}$$

where δ_β is the β component of the vector $\boldsymbol{\delta}$. Since, by Eq. (40), the left-hand side cancels the first term of the right-hand side in Eq. (41), we obtain that every term of order one and higher in the series must be identically zero:

$$\begin{aligned} &\sum_{\beta} \delta_\beta \sum_{\kappa''} \frac{\partial^2 \varepsilon_{n\mathbf{k}}}{\partial R_{\kappa'\alpha}(\boldsymbol{\Gamma}) \partial R_{\kappa''\beta}(\boldsymbol{\Gamma})}[\{\mathbf{R}_{l\kappa}\}] = 0, \quad \forall\, \delta_\beta \in \mathbb{R}, \\ &\Rightarrow \sum_{\kappa''} \frac{\partial^2 \varepsilon_{n\mathbf{k}}}{\partial R_{\kappa'\alpha}(\boldsymbol{\Gamma}) \partial R_{\kappa''\beta}(\boldsymbol{\Gamma})}[\{\mathbf{R}_{l\kappa}\}] = 0. \end{aligned} \tag{42}$$

B. The temperature dependence in the adiabatic harmonic approximation for the solid periodic case

Equation (29) can be generalized to the periodic case, with a discretized integral over $\mathbf{q}$ (N_q is the number of wave vectors used to sample the Brillouin zone):

$$\begin{aligned} \Delta\varepsilon_{n\mathbf{k}}(T) = \frac{1}{N_q} \sum_{\mathbf{q}} \sum_{m}^{3N} \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \sum_{ll'} \frac{\partial^2 \varepsilon_{n\mathbf{k}}}{\partial R_{l\kappa\alpha} \partial R_{l'\kappa'\gamma}} \\ \times e^{-i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) \left(n_{m\mathbf{q}}(T) + \frac{1}{2} \right). \end{aligned} \tag{43}$$

Similarly, the generalization of Eq. (15) leads to

$$\Delta\varepsilon_{n\mathbf{k}}(T) = \frac{1}{N_q} \sum_{\mathbf{q}} \sum_{m}^{3N} \frac{\partial \varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} \left(n_{m\mathbf{q}}(T) + \frac{1}{2} \right), \tag{44}$$

where

$$\begin{aligned} \frac{\partial \varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \sum_{ll'} \frac{\partial^2 \varepsilon_{n\mathbf{k}}}{\partial R_{l\kappa\alpha} \partial R_{l'\kappa'\gamma}} \\ \times e^{-i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}), \end{aligned} \tag{45}$$

and we will focus on the latter quantity, which represents the change of eigenenergy due to a specific phonon mode.

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the Debye-Waller term of this equation have different atomic indices κ and κ', which is not coherent with their Eq. (5) or with Ref. [46], where the polarization vectors have the same atomic index κ. On the contrary, we perfectly agree with the formulation of Giustino *et al.* [46].

To split this expression in a Fan and a Debye-Waller contribution, we substitute the extension to periodic system of Eq. (34) in it and retrieve

$$\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) \times \left\{ \langle u^{(0)}_{n\mathbf{k}} | \frac{\partial^2 \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q}) \partial R_{\kappa'\gamma}(\mathbf{q})} | u^{(0)}_{n\mathbf{k}} \rangle + \frac{1}{2} \left(\left(\left\langle \frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u^{(0)}_{n\mathbf{k}} \right\rangle + (\kappa\alpha) \leftrightarrow (\kappa'\gamma) \right) + \text{c.c.} \right) \right\}, \tag{46}$$

where $\hat{H}_{\mathbf{k},\mathbf{k}}$ is defined through Eq. (A10) applied to the Hamiltonian.

This allows us to introduce the following notation for the DW and Fan contributions related to band n and wave vector $\mathbf{k}$ (we skip the n and $\mathbf{k}$ indices, which should not be confusing in the present context):

$$\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) \triangleq \langle u^{(0)}_{n\mathbf{k}} | \frac{\partial^2 \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q}) \partial R_{\kappa'\gamma}(\mathbf{q})} | u^{(0)}_{n\mathbf{k}} \rangle, \tag{47}$$

$$\mathcal{F}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) \triangleq \frac{1}{2} \left(\left(\left\langle \frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u^{(0)}_{n\mathbf{k}} \right\rangle + (\kappa\alpha) \leftrightarrow (\kappa'\gamma) \right) + \text{c.c.} \right). \tag{48}$$

The change of eigenenergy due to a specific phonon mode, Eq. (46), thus becomes

$$\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} \triangleq \frac{\partial \varepsilon^{\text{FAN}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} + \frac{\partial \varepsilon^{\text{DW}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} \tag{49}$$

with the Fan contribution given by

$$\frac{\partial \varepsilon^{\text{FAN}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} \triangleq \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \mathcal{F}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}), \tag{50}$$

and the Debye-Waller contribution given by

$$\frac{\partial \varepsilon^{\text{DW}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} \triangleq \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}). \tag{51}$$

With the same notations, the translational invariance Eq. (42) reads

$$\sum_{\kappa'} \left(\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) + \mathcal{F}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) \right) = 0. \qquad \forall \alpha, \gamma, \kappa. \tag{52}$$

In particular, one can multiply this expression by any expression independent of κ', and still get zero. This gives us some freedom to add terms which are chosen in such a way that $\mathcal{D}$ simplifies in the rigid-ion approximation (see next section). Moreover, these supplementary terms can be chosen in such a way that the resulting expression is Hermitian:

$$\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \left\{ \left(\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) + \mathcal{F}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) \right) U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) - \frac{1}{2} \left(\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) + \mathcal{F}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) \right) \left(U^*_{m,\kappa\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) + U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa'\alpha}(\mathbf{q}) \right) \right\}. \tag{53}$$

Without loss of generality, taking advantage of the translational invariance, the Debye-Waller term is equivalently given by

$$\frac{\partial \varepsilon^{\text{DW}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \left\{ \mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) - \frac{1}{2} \left(\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) + \mathcal{F}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) \right) \left(U^*_{m,\kappa\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) + U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa'\alpha}(\mathbf{q}) \right) \right\}. \tag{54}$$

At this point, the only approximations we have used are the adiabatic and the harmonic approximations. The Debye-Waller term that we have obtained, Eq. (47), involves the second-order derivative of the first-principle Hamiltonian. In most DFPT procedures, calculations of the phonon band structure rely only on the evaluation of the *first-order* derivative of the self-consistent DFT Hamiltonian and wave functions. Indeed, while the expression leading to such phonon band structure calculations include a second-order derivative with respect to the non-self-consistent electron-ion potential, the latter term does not depend on *second-order* derivative of the wave function and Hamiltonian [48]. Thus the Debye-Waller term is not a byproduct of a phonon band structure calculation. We will now show how the rigid-ion approximation allows us to compute the Debye-Waller term without computing the second-order derivative of the self-consistent first-principles Hamiltonian.

C. The rigid-ion Hamiltonian

In the case of semiempirical potentials, it is natural to suppose that the Hamiltonian depends on potentials created

independently by each nucleus, screened by electrons attached to them. In this case, as pointed by Allen and Heine [22], the numerical burden of computing a second-order derivative of the Hamiltonian can be completely avoided. A rigid-ion Hamiltonian has the following form:

$$\hat{H}^{\mathrm{ri}} = \hat{T} + V^{\mathrm{ionic}}(\hat{\mathbf{r}}), \tag{55}$$

where

$$V^{\mathrm{ionic}}(\hat{\mathbf{r}}) = \sum_{l\kappa} V_{l\kappa}(\hat{\mathbf{r}} - \mathbf{R}_{l\kappa}). \tag{56}$$

The mixed (off-site) second-order derivatives of such Hamiltonian vanish:

$$\frac{\partial^2 \hat{H}^{\mathrm{ri}}}{\partial R_{l\kappa\alpha}\partial R_{l'\kappa'\gamma}} = 0 \qquad \text{if } \kappa \neq \kappa' \text{as well as if } l \neq l'. \tag{57}$$

Using the notation of Eq. (47), the DW term constructed with a rigid-ion Hamiltonian has the following property:

$$\mathcal{D}^{\mathrm{ri}}_{\substack{\kappa\alpha\\ \kappa'\gamma}}(\mathbf{q}) = \mathcal{D}^{\mathrm{ri}}_{\substack{\kappa\alpha\\ \kappa'\gamma}}(\mathbf{\Gamma})\delta_{\kappa,\kappa'}. \tag{58}$$

Enforcing Eq. (58) to the DW terms of Eq. (54) for a rigid-ion Hamiltonian leads to

$$\frac{\partial \varepsilon^{\mathrm{DW^{ri}}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{-1}{4\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha\\ \kappa'\gamma}} \mathcal{F}^{\mathrm{ri}}_{\substack{\kappa\alpha\\ \kappa'\gamma}}(\mathbf{\Gamma})\big(U^*_{m,\kappa\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q}) + U^*_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\big), \tag{59}$$

which is the AHC expression of the DW contribution.

D. The rigid-ion approximation

In a DFT approach (*GW* behaves similarly, with an electronic self-energy replacing the DFT exchange-correlation potential), the Hamiltonian is the sum of the kinetic energy operator $\hat{T}$ and the Kohn-Sham potential $V_{\mathrm{KS}}[\rho](\hat{\mathbf{r}})$. The latter term can further be split in the sum of potentials generated by each ion $V_{l\kappa}(\hat{\mathbf{r}} - \mathbf{R}_{l\kappa})$ and the Hartree and exchange-correlation (Hxc) potential $V_{\mathrm{Hxc}}[\rho](\hat{\mathbf{r}})$ generated by the electronic density of the system:

$$\hat{H} = \hat{T} + V_{\mathrm{KS}}[\rho](\hat{\mathbf{r}}) = \hat{T} + V_{\mathrm{ionic}}(\hat{\mathbf{r}}) + V_{\mathrm{Hxc}}[\rho](\hat{\mathbf{r}}). \tag{60}$$

Thus, the change of the Hamiltonian is related to the change of the density only through $V_{\mathrm{Hxc}}[\rho](\hat{\mathbf{r}})$. The change of the density due to the displacement of one atom being in general affected by the displacement of another atom, the second-order derivative of the Hamiltonian with respect to the displacement of two different atoms will contain contributions from $V_{\mathrm{Hxc}}[\rho](\hat{\mathbf{r}})$, but not from $\hat{T}$ and $V_{l\kappa}(\hat{\mathbf{r}} - \mathbf{R}_{l\kappa})$ since they have the form of Eq. (55). This can be seen as a consequence of the fact that, unlike the bare ionic potential, the Hxc potential is screened (see Appendix A 4 for an alternative view of the DW term expressed in term of the dielectric function).

The numerical evaluation of the Debye-Waller term is difficult since it requires the evaluation of the second functional derivative of the Hamiltonian with respect with atomic positions. A popular approximation, called the rigid-ion approximation, is to apply Eq. (59), exact for a rigid-ion Hamiltonian, to a DFT Hamiltonian:

$$\frac{\partial \varepsilon^{\mathrm{DW_{RIA}}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{-1}{4\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha\\ \kappa'\gamma}} \mathcal{F}_{\substack{\kappa\alpha\\ \kappa'\gamma}}(\mathbf{\Gamma})\big(U^*_{m,\kappa\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q}) + U^*_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\big). \tag{61}$$

With the rigid-ion approximation, the change of electronic energies reads

$$\frac{\partial \varepsilon^{\mathrm{RIA}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{\partial \varepsilon^{\mathrm{FAN}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} + \frac{\partial \varepsilon^{\mathrm{DW_{RIA}}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}}. \tag{62}$$

This rewriting makes the calculations easier to perform, since only first-order derivative of the DFT Hamiltonian have to be computed.

All Fan-like contributions can be derived from DFPT, as explained in Appendix A 3. In practice, in the AHC theory, as formulated by Giustino *et al.* [46], $\mathcal{F}_{\substack{\kappa\alpha\\ \kappa'\gamma}}(\mathbf{q})$ is obtained using Eq. (48) and

$$\left\langle \frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u^{(0)}_{n\mathbf{k}} \right\rangle = \sum_{n'=1}^{\infty}{}' \frac{\langle u^{(0)}_{n\mathbf{k}} | \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})} | u^{(0)}_{n'\mathbf{k}+\mathbf{q}} \rangle \langle u^{(0)}_{n'\mathbf{k}+\mathbf{q}} | \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} | u^{(0)}_{n\mathbf{k}} \rangle}{\varepsilon^{(0)}_{n\mathbf{k}} - \varepsilon^{(0)}_{n'\mathbf{k}+\mathbf{q}}}, \tag{63}$$

where the infinite sum over bands is truncated in numerical calculations, while the prime after the sum symbol indicates that the terms with a vanishing denominator (such situation always occurs at Γ when $n = n'$) have to be excluded.

In the resulting expression, one needs to sum over a large number of empty bands since the first-order wave function is expressed in the sum-over-states form. As shown by Sternheimer [68], the summation over highly energetic bands can be replaced by the solution of a linear equation. This equation can then be solved iteratively with the same techniques as the ones of the DFPT approach used to calculate phonon eigenvectors and eigenenergies [47,48,69,70]. The resulting expression for the first-order wave function is detailed in Appendix A 3 of this paper [Eq. (A24)] and leads to an alternative form of Eq. (63), proposed in Ref. [53]:

$$\left\langle \frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u^{(0)}_{n\mathbf{k}} \right\rangle = \sum_{n'=1}^{M}{}' \frac{\langle u^{(0)}_{n\mathbf{k}} | \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})} | u^{(0)}_{n'\mathbf{k}+\mathbf{q}} \rangle \langle u^{(0)}_{n'\mathbf{k}+\mathbf{q}} | \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} | u^{(0)}_{n\mathbf{k}} \rangle}{\varepsilon^{(0)}_{n\mathbf{k}} - \varepsilon^{(0)}_{n'\mathbf{k}+\mathbf{q}}} + \left\langle \hat{P}_{c\mathbf{k}+\mathbf{q}} \frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u^{(0)}_{n\mathbf{k}} \right\rangle. \tag{64}$$

This formulation is independent of the value of M, which is usually taken to be slightly larger than the number of bands for which the electron-phonon renormalization is sought. It removes the cumbersome sum over states, and results in a significant speed up of the calculations [53] as well as the elimination of the convergence study on the truncation of the sum. The complete expression for the change of eigenenergies

due to electron-phonon interactions, in the RIA, is obtained from the combination of Eqs. (44), (48), (50), (61), (62), and (64).

E. Beyond the rigid-ion approximation

We can now analyze the term that were neglected by enforcing the rigid-ion approximation to a general Hamiltonian. We decompose the full Debye-Waller term as follows:

$$\frac{\partial \varepsilon_{n\mathbf{k}}^{\mathrm{DW}}}{\partial n_{m\mathbf{q}}} = \frac{\partial \varepsilon_{n\mathbf{k}}^{\mathrm{DW_{RIA}}}}{\partial n_{m\mathbf{q}}} + \frac{\partial \varepsilon_{n\mathbf{k}}^{\mathrm{DW_{NRIA}}}}{\partial n_{m\mathbf{q}}}. \tag{65}$$

The second term, which we call the non-rigid-ion approximation to the Debye-Waller term, is composed of the terms neglected by the RIA:

$$\frac{\partial \varepsilon_{n\mathbf{k}}^{\mathrm{DW_{NRIA}}}}{\partial n_{m\mathbf{q}}} \triangleq \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \Big(\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) - \frac{1}{2} \mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) \times \big(U^*_{m,\kappa\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) + U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa'\alpha}(\mathbf{q}) \big) \Big). \tag{66}$$

It may be noted that the present convention differs from the one of Ref. [53]. While our FAN term is the same as Eq. (16) of this reference, our $\mathrm{DW_{RIA}}$ term is instead called *diagonal* Debye-Waller by them [see their Eq. (16)]. However, such a term is not diagonal in atom index nor in cell site, hence the new naming convention proposed here. Similarly, we may note that our $\mathrm{DW_{NRIA}}$ term is called *nondiagonal* Debye-Waller by them [see their Eq. (22)], although it possesses diagonal components.

This apparent discrepancy can be explained by noting that Ref. [53] (co-authored by some of us) studied isolated molecules, for which the only wave vector to be considered was $\mathbf{q} = \mathbf{\Gamma}$. In this context, the contribution beyond the Fan and $\mathrm{DW_{RIA}}$ was indeed purely nondiagonal. However, this is not true in the general case. Thus we believe that the updated definitions presented in this paper are more general and lifts some possible confusion.

IV. TEMPERATURE DEPENDENCE FROM FINITE DIFFERENCES OVER ATOMIC DISPLACEMENTS

The temperature dependence can also be computed through a FP approach where, in a supercell, a set of self-consistent first-principles calculations are done with atoms displaced slightly from their equilibrium positions. The change of force due to atomic displacements allows one to construct the IFC, from which the phonon frequencies and eigenvectors can be deduced.

Since the FP formalism does not include the RIA [see Eq. (61)], it becomes interesting to obtain the contributions neglected by it from FP calculations, to assess its validity.

A. The frozen-phonon approach

When performing DFPT calculations, the problem lies in the fact that the term beyond the rigid-ion approximation [Eq. (66)] requires the direct evaluation of the second-order derivative of the Hamiltonian with respect to atomic positions. Such terms might be computed by higher-order DFPT, but would require the computation of the second-order derivatives of the Hamiltonian with respect to all pairs of atomic displacements, which is prohibitive from a computational point of view. Indeed, to the author's knowledge, no solid state computer code is nowadays able to compute such terms. For this reason, we will rely on finite-difference calculations to have access to all the quantities beyond the RIA terms.

Although the IFC of Eq. (4), expressed in real space, is a symmetric matrix, the dynamical matrix $\tilde{C}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q})$ defined in Eq. (37) can be complex. First, we notice that such a quantity at $\mathbf{q}$ and $-\mathbf{q}$ is linked through time-reversal symmetry:

$$\tilde{C}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(-\mathbf{q}) = \sum_l C_{\substack{0\kappa\alpha \\ l\kappa'\gamma}} e^{-i\mathbf{q}\cdot\mathbf{R}_l} = \left(\sum_l C_{\substack{0\kappa\alpha \\ l\kappa'\gamma}} e^{+i\mathbf{q}\cdot\mathbf{R}_l} \right)^* = \tilde{C}^*_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}). \tag{67}$$

Therefore the dynamical equation for $-\mathbf{q}$ can be written as

$$\sum_{\kappa\alpha} \tilde{C}^*_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U_{m,\kappa\alpha}(-\mathbf{q}) = M_{\kappa'} \omega^2_{m-\mathbf{q}} U_{m,\kappa'\gamma}(-\mathbf{q}). \tag{68}$$

Taking the complex conjugate of the previous equation gives

$$\sum_{\kappa\alpha} \tilde{C}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U^*_{m,\kappa\alpha}(-\mathbf{q}) = M_{\kappa'} \omega^2_{m-\mathbf{q}} U^*_{m,\kappa'\gamma}(-\mathbf{q}). \tag{69}$$

Therefore, by direct comparison with Eq. (36), we can see that, for all modes m, we have $\omega^2_{m\mathbf{q}} = \omega^2_{m-\mathbf{q}}$ and $U_{m,\kappa\alpha}(\mathbf{q}) = U^*_{m,\kappa\alpha}(-\mathbf{q})$. Taking advantage of these time-reversal symmetry properties, we can define a real displacement that is the sum of a displacement at $\mathbf{q}$ and another at $-\mathbf{q}$:

$$v_{lm,\kappa\alpha}(\mathbf{q}) = \tfrac{1}{2} \big(U_{m,\kappa\alpha}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_l} + U_{m,\kappa\alpha}(-\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_l} \big), \tag{70}$$

and we can also define another real displacement that is the difference of a displacement at $\mathbf{q}$ and another at $-\mathbf{q}$:

$$w_{lm,\kappa\alpha}(\mathbf{q}) = -\tfrac{1}{2} i \big(U_{m,\kappa\alpha}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_l} - U_{m,\kappa\alpha}(-\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_l} \big). \tag{71}$$

B. Frozen-phonon expression of the different terms entering into the ZPR

Using the notation introduced in the previous section, we start from Eq. (45) and compute the second-order derivative of the eigenenergies through a FP approach based on

second-order finite differences:

$$\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\gamma}} \frac{\partial^2 \varepsilon_{n\mathbf{k}}}{\partial R_{l\kappa\alpha} \partial R_{l'\kappa'\gamma}} e^{-i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q})$$

$$= \frac{1}{2\omega_{m\mathbf{q}}} \left(\frac{\partial^2}{\partial h^2} \varepsilon_{n\mathbf{k}}[\{R_{l\kappa'\alpha} + h v_{lm,\kappa'\alpha}(\mathbf{q})\}]\big|_{h=0} + \frac{\partial^2}{\partial h^2} \varepsilon_{n\mathbf{k}}[\{R_{l\kappa'\alpha} + h w_{lm,\kappa'\alpha}(\mathbf{q})\}]\big|_{h=0} \right), \tag{72}$$

where h sets the amplitude of the FP displacement along real vector $v_{lm,\kappa\alpha}(\mathbf{q})$ or $w_{lm,\kappa\alpha}(\mathbf{q})$, $R_{l\kappa\alpha}$ are the equilibrium positions of the atoms, the eigenvalues $\varepsilon_{n\mathbf{k}}$ are evaluated with the atoms displaced along the real vector $v_{lm,\kappa\alpha}(\mathbf{q})$ or $w_{lm,\kappa\alpha}(\mathbf{q})$, and $\{\}$ denotes the set of values obtained by iterating upon l, κ, and α.

We also compute, from a FP approach, the NRIA contribution to the eigenenergies renormalization, that is, the $\mathrm{DW}_{\mathrm{NRIA}}$ contribution [Eq. (66)]

$$\frac{\partial \varepsilon^{\mathrm{DW_{NRIA}}}_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}} \left(\frac{\partial^2}{\partial h^2} \langle u^{(0)}_{n\mathbf{k}} | \hat{H}_{\mathbf{k},\mathbf{k}}[\{R_{l\kappa'\alpha} + h v_{lm,\kappa'\alpha}(\mathbf{q})\}] + \hat{H}_{\mathbf{k},\mathbf{k}}[\{R_{l\kappa'\alpha} + h w_{lm,\kappa'\alpha}(\mathbf{q})\}] | u^{(0)}_{n\mathbf{k}} \rangle \big|_{h=0} \right.$$

$$\left. - \sum_{\gamma} \frac{\partial^2}{\partial S_\gamma \partial T_\gamma} \langle u^{(0)}_{n\mathbf{k}} | \hat{V}_{\mathrm{Hxc}}[\{R_{l\kappa'\alpha} + S_\gamma U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa'\alpha}(\mathbf{q}) + T_\gamma \delta_{\alpha\gamma}\}] | u^{(0)}_{n\mathbf{k}} \rangle \big|_{S_\gamma, T_\gamma = 0} \right), \tag{73}$$

where S_γ and T_γ are scalars introduced for finite differences purposes. The term $T_\gamma \delta_{\alpha\gamma}$ computed through finite differences is a collective displacement of the atoms in a primitive cell. The derivative of this term with respect to T_γ is nonzero because the expectation value of the displaced potential is evaluated at fixed equilibrium ion position which is taken with respect to the unperturbed periodic part of the wave function $u^{(0)}_{n\mathbf{k}}$. More details on this equation can be found in Appendix A 5.

Antonius *et al.* [39] computed the temperature dependence of diamond using finite differences [Eq. (72)] in the many-body GW framework, which led to an additional 200-meV ZPR of the diamond band gap with respect to the DFT value, closer to the experimental band gap.

V. COMPARISON BETWEEN AHC/DFPT AND FINITE-DIFFERENCE RESULTS

Now that the basic framework is in place and that all the equations for the DFPT and finite-difference approach have been introduced, we can perform an actual calculation. We have chosen diamond as a test case, as it is a relatively simple but nontrivial system that has been both experimentally and theoretically thoroughly studied.

In this section, we compare AHC and FP results for some chosen $\mathbf{q}$-wave-vector contributions to the ZPR of the diamond band gap. We study the $\mathbf{q}$-wave-vector contributions to the ZPR instead of the full ZPR since the converged $\mathbf{q}$-point integration required by the full ZPR is computationally out of reach for FP. For the full $\mathbf{q}$-point integration within AHC, please see Ref. [54].

The calculation of structural properties in this work are based on density-functional theory (DFT) [29] within the local density approximation (LDA) [71,72]. We use a plane-wave basis set to represent the wave functions and account for the core-valence interaction using norm-conserving pseudopotentials [73]. The $2s^2 2p^2$ valence electrons of carbon are treated explicitly in our *ab initio* calculations. All the calculations are done using the ABINIT software package [74].

Convergence studies with a tolerance of 0.5 mHa per atom on the total energy led to the use of a $6 \times 6 \times 6$ Γ-centred Monkhorst-Pack sampling [75] of the Brillouin zone and an energy cut-off of 30 Hartree for the truncation of the plane-wave basis set. A lattice parameter of 6.675 Bohr was obtained by structural optimization.

The phonon frequencies were calculated using Eq. (5) for the DFPT method and a second-order derivative of the total energy with respect to atomic displacements converged with a Richardson interpolation of order 4, for the finite-difference method. Also, for the latter method and the $\mathbf{q} = L$ point, a $2 \times 2 \times 2$ supercell with a $3 \times 3 \times 3$ Γ-centred Monkhorst-Pack sampling were used to ensure the $\mathbf{k}$-point sampling remained equivalent to the one used for the DFPT calculation on the primitive cell. The comparison between FP and DFPT for the phonon frequencies is given in Table I. The discrepancies between the two methods remain within 0.2% for the two $\mathbf{q}$ points considered, which demonstrates both the equivalence of the two methods and the convergence of our calculations with respect to the finite difference parameter.

We now assess the accuracy of our AHC implementation and quantify the impact of the RIA. The contribution of the same two $\mathbf{q}$-points to the ZPR at $\mathbf{k} = \mathbf{\Gamma}$ and $\mathbf{k} = \mathbf{L}$ is given in Table II. This table presents the renormalization of the different eigenenergies due to electron-phonon coupling for the four first distinguishable bands of diamonds. The $\mathbf{\Gamma_{25'}}$ valence-band maximum is threefold degenerate as well as the $\mathbf{\Gamma_{15}}$ conduction band. In diamond, the conduction-band minimum is located between the $\mathbf{k} = \mathbf{\Gamma}$ and $\mathbf{k} = \mathbf{X}$ points. At the $\mathbf{k} = \mathbf{L}$, the valence $\mathbf{L_1}$ and conduction $\mathbf{L_{3'}}$ bands are only doubly degenerate. It can also be noted that our results show

TABLE I. Comparison of diamond phonon frequencies computed from FP and from DFPT.

$\mathbf{q}$ point	Mode	ω DFPT (Ha)	ω FP (Ha)	diff. (%)
$\mathbf{\Gamma}$	LO+TO	0.00606474	0.00605226	0.2058
$\mathbf{L}$	TA	0.00250256	0.00250111	0.0580
	LA	0.00494158	0.00494344	0.0376
	TO	0.00564786	0.00565244	0.0810
	LO	0.00577597	0.00577016	0.1007

TABLE II. Comparison between the AHC/DFPT and FP results for the contributions of specific **q**-points to the ZPR of several bands of diamond. The column "diff." is the sum of the AHC and the NRIA contributions minus the FP result. The % NRIA is the relative contribution of the NRIA term to the FP.

		AHC (meV)			NRIA (meV)		sum all	FP	diff.
q point	**k** point	Fan	DW_{RIA}	sum AHC	DW_{NRIA}	% NRIA	(meV)	(meV)	(μeV)
$\mathbf{\Gamma}$	$\mathbf{\Gamma_1}$	−32.8174	20.2868	−12.5306	1.4500	13.09	−11.0806	−11.0809	0.308
	$\mathbf{\Gamma_{25'}}$	−332.4265	357.2564	24.8300	3.5982	12.66	28.4282	28.4289	−0.638
	$\mathbf{\Gamma_{15}}$	−330.4363	316.2021	−14.2342	0.3848	2.78	−13.8494	−13.8497	0.338
	$\mathbf{\Gamma_{2'}}$	−63.3087	32.3760	−30.9327	0.2998	0.98	−30.6328	−30.6335	0.748
	$\mathbf{L_{2'}}$	−67.8598	46.8783	−20.9814	2.2820	12.20	−18.6993	−18.6999	0.554
	$\mathbf{L_1}$	−146.0806	129.4769	−16.6037	1.1326	7.32	−15.4710	−15.4714	0.367
	$\mathbf{L_{3'}}$	−311.2306	321.3287	10.0981	2.9610	22.67	13.0590	13.0592	−0.307
	$\mathbf{L_3}$	−473.0115	292.4656	−180.5458	0.1558	0.09	−180.3900	−180.3937	6.977
L	$\mathbf{\Gamma_1}$	−116.4278	62.6966	−53.7312	0.9068	1.72	−52.8256	−52.8245	1.104
	$\mathbf{\Gamma_{25'}}$	−922.8240	1104.1052	181.2812	2.2949	1.25	183.5761	183.5771	−1.017
	$\mathbf{\Gamma_{15}}$	−1250.8082	977.2263	−273.5819	−1.0060	0.37	−274.5878	−274.5881	0.244
	$\mathbf{\Gamma_{2'}}$	−407.6022	100.0584	−307.5438	−1.8483	0.60	−309.3921	−309.3973	5.131
	$\mathbf{L_{2'}}$	−234.2353	144.8781	−89.3572	1.4860	1.69	−87.8712	−87.8728	1.542
	$\mathbf{L_1}$	−620.7070	400.1500	−220.5570	0.5069	0.23	−220.0501	−220.0525	2.359
	$\mathbf{L_{3'}}$	−1018.9788	993.0698	−25.9090	1.7417	7.21	−24.1674	−24.1672	−0.210
	$\mathbf{L_3}$	−740.6821	903.8683	163.1862	−1.0928	0.67	162.0934	162.0935	−0.142

the contribution of some **q** points to the ZPR with values in very close agreements (within 2 meV) with Fig. 1 of Ref. [39] that shows the electron-phonon coupling energies (there is therefore a conversion factor of 1/2).

The AHC results are split into Fan and DW_{RIA} contributions that are computed using Eqs. (50) and (61), respectively. The importance of the rigid-ion approximation can be deduced by computing the DW_{NRIA} term through finite difference calculations using Eq. (73).

The impact of the RIA remains below 23% and is usually much smaller for wavevectors other than the zone-center one. To assess completely the validity of the approximation, we should do a full **q**-point integration on the BZ. However, since the ZPR converges extremely slowly with the number of **q** points [54], this would require huge supercell calculations, which are currently computationally out of reach.

Finally, the sum of the AHC and NRIA contributions can be compared to the finite difference calculations done using Eq. (72). All the FP calculations are also converged with a Richardson interpolation of order 4. The discrepancies remain below 7 μeV in absolute value. Such discrepancies can be attributed to numerical noise or anharmonicity. Indeed, the finite displacements selected in the FP method (0.02 to 0.0025 Bohr) ensure a good compromise between these two sources of error, so that both are present, but as small as allowed by our convergence criterion.

VI. CONCLUSIONS

The renormalization of eigenenergies due to electron-phonon coupling can be computed by different methods. In this paper, we have reviewed three of them: the first-principles molecular dynamics method, the frozen-phonon (FP) method, and the Allen-Heine-Cardona (AHC) method based on density-functional perturbation theory. The two first methods are equivalent within the adiabatic harmonic approximation while the third is only equivalent when the non-rigid-ion (NRIA) terms are included or when the rigid-ion approximation (RIA) is valid.

The theory's key ingredient is the second-order derivative of the eigenenergies with respect to two atomic displacements. This derivative splits into a term involving the first-order modification of the wave function (the Fan term) and a term corresponding to a second-order perturbation of the Hamiltonian [the Debye-Waller (DW) term]. Although the two terms were discovered separately in the 50's, there was a lot of confusion in the literature until Baumann realised in 1974 the complementarity of these two terms for the computation of the zero-point motion renormalization (ZPR).

The present paper compared in detail two (AHC/DFPT and FP) of the three approaches still used today to calculate the ZPR. We considered the first for its efficiency in the computation of the ZPR at arbitrary **q** points, crucial for periodic system, and the later, to go beyond the RIA and study its impact on the calculated ZPR.

Also, in this paper, we derived Brook's theorem in the first-principle context and obtained an expression for the eigenenergy renormalization from the finite temperature extension of Janak's theorem [see Eqs. (31) and (24)]. We also rederived how, within the RIA, the translational invariance [Eq. (42)] allows to express the DW contribution in terms of first-order derivatives of the Hamiltonian only.

A major contribution of this paper is the clarification of the term appearing beyond the RIA made in the AHC theory. This allows all the definitions to be coherent with their respective names [see Eqs. (50), (61), and (66)]. Nevertheless, due to the computational limitation related to the evaluation of the second-order derivative of the Hamiltonian, the NRIA terms cannot be computed with DFPT, as implemented now. Therefore we derived the equations related to the FP approach,

which allows us to numerically evaluate the NRIA terms in the case of bulk diamond [see Eqs. (72) and (73)].

For the diamond phonon frequencies, the maximum discrepancy between the FP and AHC approaches is below 0.2%. The differences of ZPR between the two methods are always below 7 μeV in absolute value, which strengthens our confidence in the theory and numerical implementation within the ABINIT software. These small differences are attributed to the unavoidable numerical noise and anharmonicity in the FP calculations. The impact of the RIA is also evaluated for two **q** points ($\mathbf{\Gamma}$ and **L**) and is found to be as large as 23% for the Γ zone center contribution to the ZPR but is usually much smaller for other **q**-point contributions.

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APPENDIX: TECHNICALITIES

1. Integrals of phonon wave functions and powers of the position operator

We evaluate the integrals present in Eq. (7), with the Taylor expansion of the eigenenergy. In the harmonic approximation, the phonon wave functions are obtained by solving the Schrödinger equation for the harmonic oscillator. We obtain [76]

$$\chi_{s_m,m}(z) = \left(\frac{\omega_m}{\pi}\right)^{1/4} \frac{H_{s_m}(\xi)}{\sqrt{2^{s_m} s_m!}} e^{-\frac{\xi^2}{2}}, \tag{A1}$$

where $H_{s_m}(\xi) = (-1)^{s_m} e^{\xi^2} \frac{d^{s_m}}{d\xi^{s_m}} e^{-\xi^2}$ is the Hermite polynomial and $\xi = \sqrt{\omega_m} z$ is a dimensionless position variable. Hermite polynomials satisfy the following orthonormality condition:

$$\int H_p(\xi) H_{s_m}(\xi) e^{-\xi^2} d\xi = s_m! \sqrt{\pi} 2^{s_m} \delta_{p s_m}. \tag{A2}$$

The phonon wave functions are thus normalized, with

$$\int \chi_{s_m,m}(z)^* \chi_{s_m,m}(z) dz = 1. \tag{A3}$$

The first-order integral cancels out, as an odd function integrates to zero:

$$\int \chi_{s_m,m}(z)^* z \chi_{s_m,m}(z) dz = 0. \tag{A4}$$

Finally, the second-order integral can easily be solved in second quantization using

$$|\chi_{s_m,m}\rangle = \frac{(a^+)^{s_m}}{\sqrt{s_m!}} |0\rangle, \quad \xi^2 = \frac{1}{2}(a + a^+)^2. \tag{A5}$$

We thus obtain

$$\begin{aligned}
&\int \chi_{s_m,m}(z)^* z^2 \chi_{s_m,m}(z) dz \\
&= \frac{1}{\omega_m} \langle \chi_{s_m,m} | \xi^2 | \chi_{s_m,m} \rangle \\
&= \frac{1}{\omega_m s_m!} \langle 0 | a^{s_m} \frac{1}{2}(a + a^+)^2 (a^+)^{s_m} | 0 \rangle \\
&= \frac{1}{\omega_m s_m!} \langle 0 | a^{s_m} \frac{1}{2}(a a^+ + a^+ a)(a^+)^{s_m} | 0 \rangle \\
&= \frac{1}{\omega_m s_m!} \langle 0 | a^{s_m} \frac{1}{2}(2 a a^+ - 1)(a^+)^{s_m} | 0 \rangle \\
&= \frac{1}{\omega_m s_m!} \left(\langle 0 | a^{s_m+1} (a^+)^{s_m+1} | 0 \rangle - \frac{1}{2} \langle 0 | a^{s_m} (a^+)^{s_m} | 0 \rangle \right) \\
&= \frac{1}{\omega_m s_m!} \left((s_m + 1)! - \frac{1}{2} s_m! \right) = \left(\frac{2 s_m + 1}{2 \omega_m} \right).
\end{aligned} \tag{A6}$$

2. Convention for the unperturbed periodic system

Following the same convention as Gonze [48], the unperturbed wave function can be obtained as the product of a phase factor and a periodic function (Bloch's theorem):

$$\Psi^{(0)}_{n\mathbf{k}}(\mathbf{r}) = (N_{\mathrm{BvK}} \Omega_0)^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} u^{(0)}_{n\mathbf{k}}(\mathbf{r}), \tag{A7}$$

where N_{BvK} is the number of unit cells repeated in the Born-von Karman periodic box, Ω_0 the volume of the unperturbed unit cell, n the band index and **k** label the wave vector of the wave function.

The periodic part of the Bloch wave function, in Eq. (A7), is subject to the following orthonormalization condition:

$$\left\langle u^{(0)}_{n'\mathbf{k}} \middle| u^{(0)}_{n\mathbf{k}} \right\rangle = \delta_{n'n}, \tag{A8}$$

where the scalar product of periodic functions is defined as

$$\langle f | g \rangle = \frac{1}{\Omega_0} \int_{\Omega_0} f^*(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}. \tag{A9}$$

For a generic operator, we follow the following convention:

$$O_{\mathbf{k},\mathbf{k}'} = e^{-i\mathbf{k}\cdot\mathbf{r}} O e^{-i\mathbf{k}'\cdot\mathbf{r}'}. \tag{A10}$$

3. Perturbation theory

The perturbation theory for a periodic system is based on the idea that the solution of a reference system (usually the equilibrium ground state one-body Schrödinger equation) is known. In general, the perturbation can be incommensurate with the periodic system and characterized by a wave vector **q**. If the amplitude of the perturbation is characterized by a small scalar parameter λ, then any observable $X(\lambda)$ can be

expressed as a power series:

$$X(\lambda) = X^{(0)} + \left(\lambda X^{(1)}_{\mathbf{q}} + \lambda^* X^{(1)}_{-\mathbf{q}}\right) + \left(\lambda^2 X^{(2)}_{\mathbf{q},\mathbf{q}} + \lambda\lambda^* X^{(2)}_{\mathbf{q},-\mathbf{q}} + \lambda^*\lambda X^{(2)}_{-\mathbf{q},\mathbf{q}} + \lambda^{*2} X^{(2)}_{-\mathbf{q},-\mathbf{q}}\right) + \cdots, \quad \text{(A11)}$$

where we use the superscript notation as a shorthand for derivatives: $X^{(i)}_{\mathbf{q}} = d^i X_{\mathbf{q}}/i!d\lambda^i|_{\lambda=0}$. The perturbed Schrödinger equation now depends explicitly on the parameter λ:

$$H(\lambda)\,|\Psi_{n\mathbf{k}}(\lambda)\rangle = \varepsilon_{n\mathbf{k}}(\lambda)\,|\Psi_{n\mathbf{k}}(\lambda)\rangle\,, \quad \text{(A12)}$$

where n is the band index and $\mathbf{k}$ is a wave vector in the Brillouin zone. The solutions $|\Psi_{n\mathbf{k}}(\lambda)\rangle$ must fulfill the normalization condition $\langle\Psi_{n\mathbf{k}}(\lambda)|\Psi_{n\mathbf{k}}(\lambda)\rangle = 1$. The Hamiltonian $\hat{H}(\lambda)$ depends parametrically on the atomic position $\mathbf{R}_{l\kappa}$ of the atom κ in the cell l.

The translated first-order wave function becomes

$$\Psi^{(1)}_{n\mathbf{k},\mathbf{q}}(\mathbf{r}+\mathbf{R}_a) = e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_a}\Psi^{(1)}_{n\mathbf{k},\mathbf{q}}(\mathbf{r}), \quad \text{(A13)}$$

where $\mathbf{R}_a$ is a vector of the real space lattice. We can then factorize out the phase factor to map the incommensurate problem into a problem commensurate with periodicity of the unperturbed one. To this end, we introduce the periodic first-order wave functions

$$u^{(1)}_{n\mathbf{k},\mathbf{q}} = (N_{\mathrm{BvK}}\Omega_0)^{1/2} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}\Psi^{(1)}_{n\mathbf{k},\mathbf{q}}(\mathbf{r}). \quad \text{(A14)}$$

We define $S_{M\mathbf{k}+\mathbf{q}}$ as the space of the M lowest-lying $\mathbf{k}+\mathbf{q}$ unperturbed states, M being larger or equal to the index of the highest band for which we aim to compute the temperature-dependent behavior. We define $P_{M\mathbf{k}+\mathbf{q}}$ as the projector on $S_{M\mathbf{k}+\mathbf{q}}$. We also define $P_{c\mathbf{k}+\mathbf{q}}$ as the projector on the subspace of $\mathbf{k}+\mathbf{q}$ ground-state wave functions complementary to $S_{M\mathbf{k}+\mathbf{q}}$. The first-order derivatives of wave functions can be split in two contributions, one that is contained inside $S_{M\mathbf{k}+\mathbf{q}}$ and one that belongs to its complement,

$$\left|u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle = \left|P_{M\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle + \left|P_{c\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle. \quad \text{(A15)}$$

$|P_{M\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\rangle$ can be easily computed using standard perturbation theory,

$$\left|P_{M\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle = -\sum_{n'}^{M}\frac{\left|u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right\rangle\left\langle u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right|H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\left|u^{(0)}_{n\mathbf{k}}\right\rangle}{\varepsilon^{(0)}_{n'\mathbf{k}+\mathbf{q}} - \varepsilon^{(0)}_{n\mathbf{k}}}. \quad \text{(A16)}$$

For $|P_{c,\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\rangle$, we want to avoid the summation over an infinite number of states. So, in the spirit of DFPT, we minimize

$$E^{(2)+}_{-\mathbf{q},\mathbf{q}}\{u^{(0)},u^{(1)}\} = E^{(2)}_{-\mathbf{q},\mathbf{q}}\{u^{(0)},u^{(1)}\} - \sum_{nn'}^{MM}\Lambda_{nn'\mathbf{k},\mathbf{k}+\mathbf{q}}\left\langle u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right|P_{c\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\rangle + \text{c.c.}, \quad \text{(A17)}$$

where $E^{(2)}_{-\mathbf{q},\mathbf{q}}\{u^{(0)},u^{(1)}\}$ is given in Eq. (42) of Ref. [48], under the constraint of parallel-transport gauge [77],

$$\left\langle u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right|P_{c\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\rangle = 0, \quad \text{(A18)}$$

with the Lagrange parameters

$$\Lambda^*_{nn'\mathbf{k},\mathbf{k}+\mathbf{q}} = \Lambda_{n'n\mathbf{k}+\mathbf{q},\mathbf{k}}. \quad \text{(A19)}$$

The minimum of this expression with respect to variations of $P_{c\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}$ leads to the canonical Euler-Lagrange equation

$$\left(H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}} - \varepsilon^{(0)}_{n\mathbf{k}}\right)\left|P_{c\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle = -H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\left|u^{(0)}_{n\mathbf{k}}\right\rangle + \sum_{n'}\Lambda^*_{nn'\mathbf{k},\mathbf{k}+\mathbf{q}}\left|u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right\rangle. \quad \text{(A20)}$$

We can then premultiply on each side by $\langle u^{(0)}_{n''\mathbf{k}+\mathbf{q}}|$ where $n'' \in [1,M]$ and get

$$\left(\varepsilon^{(0)}_{n''\mathbf{k}+\mathbf{q}} - \varepsilon^{(0)}_{n\mathbf{k}}\right)\overbrace{\left\langle u^{(0)}_{n''\mathbf{k}+\mathbf{q}}\middle|u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle}^{=0 \text{ due to Eq. (A18)}} + \left\langle u^{(0)}_{n''\mathbf{k}+\mathbf{q}}\right|H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\left|u^{(0)}_{n\mathbf{k}}\right\rangle = \sum_{n'}\Lambda^*_{nn'\mathbf{k},\mathbf{k}+\mathbf{q}}\underbrace{\left\langle u^{(0)}_{n''\mathbf{k}+\mathbf{q}}\middle|u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right\rangle}_{\delta_{n''n'}}. \quad \text{(A21)}$$

This leads to the equation

$$\Lambda^*_{nn''\mathbf{k}+\mathbf{q},\mathbf{k}} = \left\langle u^{(0)}_{n''\mathbf{k}+\mathbf{q}}\right|H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\left|u^{(0)}_{n\mathbf{k}}\right\rangle. \quad \text{(A22)}$$

We can then substitute Eq. (A22) inside Eq. (A20) and get

$$\left(H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}} - \varepsilon^{(0)}_{n\mathbf{k},\mathbf{q}}\right)\left|P_{c\mathbf{k}+\mathbf{q}}u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle = -\underbrace{\left(1 - \sum_{n'}^{N_{\max}}\left|u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right\rangle\left\langle u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right|\right)}_{P_{c\mathbf{k}+\mathbf{q}}}H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\left|u^{(0)}_{n\mathbf{k}}\right\rangle, \quad \text{(A23)}$$

and finally,

$$P_{c,\mathbf{k}+\mathbf{q}}\left(H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}} - \varepsilon^{(0)}_{n\mathbf{k}}\right)P_{c,\mathbf{k}+\mathbf{q}}\left|u^{(1)}_{n\mathbf{k},\mathbf{q}}\right\rangle = -P_{c,\mathbf{k}+\mathbf{q}}H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}\left|u^{(0)}_{n\mathbf{k}}\right\rangle. \quad \text{(A24)}$$

Supposing $H^{(1)}$ has already be determined by the usual DFPT self-consistency loop over occupied states only (in which $M = N_{val}$), the $u^{(1)}_{n\mathbf{k},\mathbf{q}}$ are found by solving Eq. (A24), combined with Eqs. (A15) and (A16).

4. The static electronic dielectric function

The DW term involves the second-order derivative with respect to atomic displacements of the Hamiltonian and as such only depends on $V_{\mathrm{KS}}[\rho](\hat{\mathbf{r}})$. We can use the static electronic dielectric function $\hat{\epsilon}$ to have an alternative physical view on the DW term. To treat integrals rigorously, we apply the position operators of a function f onto their respective bra and ket $f(\mathbf{r}) = \langle\mathbf{r}|f(\hat{\mathbf{r}})|\mathbf{r}\rangle$ and get

$$\frac{\partial V_{\mathrm{KS}}[\rho](\mathbf{r})}{\partial R_{l\kappa\alpha}} = \int \epsilon^{-1}(\mathbf{r},\mathbf{r}')\frac{\partial V_{\mathrm{ionic}}(\mathbf{r}')}{\partial R_{l\kappa\alpha}}d\mathbf{r}' \quad \text{(A25)}$$

$$= \int \epsilon^{-1}(\mathbf{r},\mathbf{r}')\frac{\partial V_{l\kappa\alpha}}{\partial R_{l\kappa\alpha}}\bigg|_{\mathbf{r}'-R_{l\kappa\alpha}}d\mathbf{r}', \quad \text{(A26)}$$

with

$$\epsilon^{-1}(\mathbf{r},\mathbf{r}') = \frac{\partial V_{\mathrm{KS}}[\rho](\mathbf{r})}{\partial V_{\mathrm{ionic}}(\mathbf{r}')}. \quad \text{(A27)}$$

Equation (A26) can then be derived a second time to give the DW term

$$\frac{\partial^2 V_{\mathrm{KS}}[\rho](\mathbf{r})}{\partial R_{l\kappa\alpha}\partial R_{l'\kappa'\gamma}} = \int \frac{\partial \epsilon^{-1}(\mathbf{r},\mathbf{r}')}{\partial R_{l'\kappa'\gamma}} \frac{\partial V_{l\kappa\alpha}}{\partial R_{l\kappa\alpha}}\bigg|_{\mathbf{r}'-R_{l\kappa\alpha}} d\mathbf{r}' + \int \epsilon^{-1}(\mathbf{r},\mathbf{r}') \frac{\partial^2 V_{l\kappa\alpha}}{\partial R_{l\kappa\alpha}\partial R_{l'\kappa'\gamma}}\bigg|_{\mathbf{r}'-R_{l\kappa\alpha}} \delta_{\kappa\kappa'}\delta_{ll'} d\mathbf{r}', \quad \text{(A28)}$$

where there is a $\delta_{\kappa\kappa'}\delta_{ll'}$ appearing in the second part of the equation because the ionic potential is a sum of separate contributions depending only on one atomic position (therefore its second derivative with respect to two different atoms positions is zero). From this equation, one can see that the first term has off-diagonal contributions in κ,κ' (beyond RIA). It is unfortunately not possible to map the diagonal contributions of Eq. (A28) to the rigid-ion DW term of Eq. (61) nor the nondiagonal contributions to the non-rigid-ion DW term of Eq. (66).

5. Development of Eq. (73)

In this section, we focus on how to obtain the finite-difference expression given in Eq. (73) from the definition of $\frac{\partial \varepsilon_{n\mathbf{k}}^{\mathrm{DW_{NRIA}}}}{\partial n_{m\mathbf{q}}}$ that was introduced in Eq. (66). The later expression contains two terms. Let us first focus on the first one.

Following the same approach used to derive Eq. (72), we can obtain a finite-difference version of the second-order derivative of the form

$$\langle u_{n\mathbf{k}}^{(0)}| \frac{\partial^2 \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})\partial R_{\kappa\gamma}(\mathbf{q})} |u_{n\mathbf{k}}^{(0)}\rangle U_{m,\kappa\gamma}^*(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) = \frac{\partial^2}{\partial h^2} \langle u_{n\mathbf{k}}| \hat{H}_{\mathbf{k},\mathbf{k}}[\{R_{l\kappa'\alpha} + h v_{lm,\kappa\alpha}(\mathbf{q})\}] + \hat{H}_{\mathbf{k},\mathbf{k}}[\{R_{l\kappa'\alpha} + h w_{lm,\kappa\alpha}(\mathbf{q})\}] |u_{n\mathbf{k}}^{(0)}\rangle\big|_{h=0}. \quad \text{(A29)}$$

It is worthwhile to dwell into the reasons for keeping the full Hamiltonian. As introduced in Eq. (60), the Hamiltonian is the sum of an electronic kinetic energy $\hat{T}$, an external potential $V_{l\kappa}(\hat{\mathbf{r}} - \mathbf{R}_{l\kappa})$ that describes the electron-ion interaction and an Hartree and exchange-correlation $\hat{V}_{\mathrm{Hxc}}[\rho](\hat{\mathbf{r}})$ potential that describes the electron-electron interactions. Within the adiabatic approximation, the kinetic energy is independent of atomic position. The second-order derivative of the Hartree and exchange-correlation with respect to atomic positions is, however, nonzero, in general, due to the modification of the electronic density upon second-order ionic motion. Furthermore, the second-order derivative of the external potential is zero when $\kappa \neq \kappa'$ since the potential only depends on one atomic coordinate. When $\kappa = \kappa'$, the external potential part of the first term in Eq. (73) is zero only when

$$\mathbf{q} = \alpha b_1 + \beta b_2 + \gamma b_3 \quad \text{with } \alpha = \beta = \gamma = n/2, \quad \text{(A30)}$$

with n an integer number and b_1, b_2, b_3 being the reciprocal lattice vectors.

To demonstrate the latter statement, we define $\mathbf{y} \triangleq \hat{\mathbf{r}} - \mathbf{R}_{l\kappa} - h_\kappa \mathbf{U}_{m,\kappa}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_l}$ and $\tilde{\mathbf{y}} \triangleq \hat{\mathbf{r}} - \mathbf{R}_{l\kappa} - h_\kappa \mathbf{U}_{m,\kappa}(\mathbf{q})$. Then the external potential becomes

$$\frac{\partial^2}{\partial h_\kappa^2} \langle u_{n\mathbf{k}}^{(0)}| \sum_{l\kappa} V_{l\kappa}(\mathbf{y}) - V_{l\kappa}(\tilde{\mathbf{y}}) |u_{n\mathbf{k}}^{(0)}\rangle\big|_{h_\kappa=0} = \frac{\partial}{\partial h_\kappa} \langle u_{n\mathbf{k}}^{(0)}| \sum_{l\kappa} \frac{\partial V_{l\kappa}(\mathbf{y})}{\partial \mathbf{y}} \cdot \frac{\partial \mathbf{y}}{\partial h_\kappa} - \frac{\partial V_{l\kappa}(\tilde{\mathbf{y}})}{\partial \tilde{\mathbf{y}}} \cdot \frac{\partial \tilde{\mathbf{y}}}{\partial h_\kappa} |u_{n\mathbf{k}}^{(0)}\rangle\big|_{h_\kappa=0}. \quad \text{(A31)}$$

This in turn gives

$$\frac{\partial}{\partial h_\kappa} \langle u_{n\mathbf{k}}^{(0)}| \sum_{l\kappa} -\frac{V_{l\kappa}(\mathbf{y})}{\partial \mathbf{y}} \cdot \mathbf{U}_{m,\kappa}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_l} + \frac{\partial V_{l\kappa}(\tilde{\mathbf{y}})}{\partial \tilde{\mathbf{y}}} \cdot \mathbf{U}_{m,\kappa}(\mathbf{q}) |u_{n\mathbf{k}}^{(0)}\rangle\big|_{h_\kappa=0} = \langle u_{n\mathbf{k}}^{(0)}| \sum_{l\kappa\alpha\beta} \frac{\partial^2 V_{l\kappa}(\hat{\mathbf{r}} - \mathbf{R}_{l\kappa}^{(0)})}{\partial(\hat{\mathbf{r}} - \mathbf{R}_{l\kappa})_\alpha \partial(\hat{\mathbf{r}} - \mathbf{R}_{l\kappa})_\beta} \times U_{m,\kappa\alpha}(\mathbf{q}) U_{m,\kappa\beta}(\mathbf{q}) (e^{2i\mathbf{q}\cdot\mathbf{R}_l} - 1) |u_{n\mathbf{k}}^{(0)}\rangle, \quad \text{(A32)}$$

where, for the last equality, we have taken the limit of vanishing h_κ. This is the reason why the Hamiltonian appears in the first terms of Eq. (73) while the last term (in which the DW term is evaluate at $\mathbf{q} = \mathbf{\Gamma}$) involves only $\hat{V}_{\mathrm{Hxc}}$.

We now evaluate the second term of Eq. (66). To this end, we introduce a collective translational displacement in the γ direction:

$$\frac{\partial}{\partial T_\gamma} \triangleq \sum_{\kappa'} \frac{\partial}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})} \quad \text{(A33)}$$

and a second-order displacement vector of the atom κ in the direction α and γ:

$$\frac{\partial}{\partial S_\gamma} \triangleq \sum_{\kappa\alpha} U_{m,\kappa\gamma}^*(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) \frac{\partial}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}. \quad \text{(A34)}$$

We therefore have the following relation:

$$\sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \langle u_{n\mathbf{k}}^{(0)}| \frac{\partial^2 \hat{V}_{\mathrm{Hxc}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma}) \partial R_{\kappa'\gamma}(\mathbf{\Gamma})} |u_{n\mathbf{k}}^{(0)}\rangle U_{m,\kappa\gamma}^*(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) = \sum_\gamma \langle u_{n\mathbf{k}}^{(0)}| \frac{\partial^2 \hat{V}_{\mathrm{Hxc}}}{\partial S_\gamma \partial T_\gamma} |u_{n\mathbf{k}}^{(0)}\rangle. \quad \text{(A35)}$$

[1] W. G. Aulbur, L. Jönsson, and J. W. Wilkins, in *Quasiparticle Calculations in Solids*, Solid State Physics Vol. 54 (Academic Press, New York, 1999), pp. 1–218.

[2] M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. **99**, 246403 (2007).

[3] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[4] C. D. Clark, P. J. Dean, and P. V. Harris, Proc. R. Soc. London, Ser. A **277** (1964).

[5] M. Cardona, Solid State Commun. **133**, 3 (2005).

[6] W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950).
[7] H. Fröhlich, H. Pelzer, and S. Zienau, Phil. Mag. **41**, 221 (1950).
[8] H. Fröhlich, Proc. R. Soc. Lond. A **215**, 291 (1952).
[9] H. Fröhlich, Adv. Phys. **3**, 325 (1954).
[10] R. van Leeuwen, Phys. Rev. B **69**, 115110 (2004).
[11] H. Y. Fan, Phys. Rev. **78**, 808 (1950).
[12] H. Y. Fan, Phys. Rev. **82**, 900 (1951).
[13] M. L. Cohen, Phys. Rev. **128**, 131 (1962).
[14] E. Antončík, Cechoslovackij Fiziceskij Zurnal **5**, 449 (1955).
[15] C. Keffer, T. M. Hayes, and A. Bienenstock, Phys. Rev. Lett. **21**, 1676 (1968).
[16] J. P. Walter, R. R. L. Zucca, M. L. Cohen, and Y. R. Shen, Phys. Rev. Lett. **24**, 102 (1970).
[17] R. V. Kasowski, Phys. Rev. B **8**, 1378 (1973).
[18] H. Brooks, in *Theory of the Electrical Properties of Germanium and Silicon*, Advances in Electronics and Electron Physics Vol. 7 (Academic Press, New York, 1955), pp. 85–182.
[19] P. B. Allen and J. C. K. Hui, Zeitschrift für Physik B Condens. Matter **37**, 33 (1980).
[20] R. D. King-Smith, R. J. Needs, V. Heine, and M. J. Hodgson, Europhys. Lett. **10**, 569 (1989).
[21] K. Baumann, Physica Status Solidi (b) **63**, K71 (1974).
[22] P. B. Allen and V. Heine, J. Phys. C **9**, 2305 (1976).
[23] P. B. Allen and M. Cardona, Phys. Rev. B **23**, 1495 (1981).
[24] P. B. Allen and M. Cardona, Phys. Rev. B **27**, 4760 (1983).
[25] P. Lautenschlager, P. B. Allen, and M. Cardona, Phys. Rev. B **31**, 2163 (1985).
[26] S. Zollner, M. Cardona, and S. Gopalan, Phys. Rev. B **45**, 3376 (1992).
[27] V. Heine and J. A. Van Vechten, Phys. Rev. B **13**, 1622 (1976).
[28] J. V. Vechten, R. Tsu, F. Saris, and D. Hoonhout, Phys. Lett. A **74**, 417 (1979).
[29] R. M. Martin, *Electronic Structure. Basic Theory and Practical Methods* (Cambridge University Press, New York, 2004).
[30] A. Franceschetti, Phys. Rev. B **76**, 161301 (2007).
[31] H. Kamisaka, S. V. Kilina, K. Yamashita, and O. V. Prezhdo, J. Phys. Chem. C **112**, 7800 (2008).
[32] Z. A. Ibrahim, A. I. Shkrebtii, M. J. G. Lee, K. Vynck, T. Teatro, W. Richter, T. Trepk, and T. Zettler, Phys. Rev. B **77**, 125218 (2008).
[33] R. Ramírez, C. P. Herrero, and E. R. Hernández, Phys. Rev. B **73**, 245202 (2006).
[34] R. Ramírez, C. P. Herrero, E. R. Hernández, and M. Cardona, Phys. Rev. B **77**, 045210 (2008).
[35] R. B. Capaz, C. D. Spataru, P. Tangney, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **94**, 036801 (2005).
[36] C. E. Patrick and F. Giustino, Nat. Commun. **4** (2013).
[37] P. Han and G. Bester, Phys. Rev. B **88**, 165311 (2013).
[38] B. Monserrat, N. D. Drummond, and R. J. Needs, Phys. Rev. B **87**, 144302 (2013).
[39] G. Antonius, S. Poncé, P. Boulanger, M. Côté, and X. Gonze, Phys. Rev. Lett. **112**, 215501 (2014).
[40] M. Lazzeri, C. Attaccalite, L. Wirtz, and F. Mauri, Phys. Rev. B **78**, 081406 (2008).
[41] A. Grüneis, J. Serrano, A. Bosak, M. Lazzeri, S. L. Molodtsov, L. Wirtz, C. Attaccalite, M. Krisch, A. Rubio, F. Mauri *et al.*, Phys. Rev. B **80**, 085423 (2009).
[42] J. Laflamme Janssen, M. Côté, S. G. Louie, and M. L. Cohen, Phys. Rev. B **81**, 073106 (2010).
[43] C. Faber, J. L. Janssen, M. Côté, E. Runge, and X. Blase, Phys. Rev. B **84**, 155104 (2011).
[44] S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, and S. Fratini, Phys. Rev. Lett. **108**, 256401 (2012).
[45] Z. P. Yin, A. Kutepov, and G. Kotliar, Phys. Rev. X **3**, 021011 (2013).
[46] F. Giustino, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **105**, 265501 (2010).
[47] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).
[48] X. Gonze, Phys. Rev. B **55**, 10337 (1997).
[49] A. Marini, Phys. Rev. Lett. **101**, 106405 (2008).
[50] E. Cannuccia and A. Marini, Phys. Rev. Lett. **107**, 255501 (2011).
[51] E. Cannuccia and A. Marini, Eur. Phys. J. B **85**, 1 (2012).
[52] H. Kawai, K. Yamashita, E. Cannuccia, and A. Marini, Phys. Rev. B **89**, 085202 (2014).
[53] X. Gonze, P. Boulanger, and M. Côté, Annalen der Physik **523**, 168 (2011).
[54] S. Poncé, G. Antonius, P. Boulanger, E. Cannuccia, A. Marini, M. Côté, and X. Gonze, Comp. Mater. Sci. **83**, 341 (2014).
[55] P. Lautenschlager, P. B. Allen, and M. Cardona, Phys. Rev. B **33**, 5501 (1986).
[56] S. Gopalan, P. Lautenschlager, and M. Cardona, Phys. Rev. B **35**, 5577 (1987).
[57] F. Giustino, M. L. Cohen, and S. G. Louie, Phys. Rev. B **76**, 165108 (2007).
[58] O. D. Restrepo, K. Varga, and S. T. Pantelides, Appl. Phys. Lett. **94**, 212103 (2009).
[59] O. D. Restrepo and W. Windl, Phys. Rev. Lett. **109**, 166604 (2012).
[60] X. Gonze and C. Lee, Phys. Rev. B **55**, 10355 (1997).
[61] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).
[62] B. Fultz, Prog. Mater. Sci. **55**, 247 (2010).
[63] N. D. Mermin, Phys. Rev. **137**, A1441 (1965).
[64] H. Hellmann, *Einführung in die Quantenchemie* (Leipzig: Franz Deuticke, 1937), p. 285.
[65] R. P. Feynman, Phys. Rev. **56**, 340 (1939).
[66] S. Yu, Ph.D. thesis, Harvard University, 1964.
[67] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).
[68] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).
[69] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
[70] X. Gonze, Zeitschrift für Kristallographie **220**, 558 (2005).
[71] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[72] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[73] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[74] X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côté *et al.*, Comp. Phys. Commun. **180**, 2582 (2009).
[75] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[76] D. J. Griffiths, *Introduction to Quantum Mechanics* (Pearson Prentice Hall, Upper Saddle River, NJ, 1995).
[77] X. Gonze, Phys. Rev. A **52**, 1096 (1995).
[78] G.-M. Rignanese, J.-P. Michenaud, and X. Gonze, Phys. Rev. B **53**, 4488 (1996).